

**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

Mo6862/LeA 33,590

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

**10/019578**  
To Be Assigned

INTERNATIONAL APPLICATION NO.

PCT/EP00/05392

INTERNATIONAL FILING DATE

June 13, 2000

PRIORITY DATE CLAIMED

June 25, 1999

TITLE OF INVENTION

Condensation Corss-Linking Polyurethane Materials Containing Special Aminosilanes, A Method For The Production Thereof And Their Use

APPLICANT(S) FOR DO/EO/US Lutz Schmalstieg, Ralf Lemmerz, Ulrich Walter (Deceased), Oswald Wilmes

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☒ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
- ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
- ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

**Items 11 to 20 below concern document(s) or information included:**

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

Certificate of Inheritance and Certified Copy thereof

Abstract

Form PTO 1449 w/rerferences

21. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**Neither international preliminary examination fee (37 CFR 1.482)  
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO  
and International Search Report not prepared by the EPO or JPO. . . . . \$1040.00International preliminary examination fee (37 CFR 1.482) not paid to  
USPTO but International Search Report prepared by the EPO or JPO . . . . . \$890.00International preliminary examination fee (37 CFR 1.482) not paid to USPTO  
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . . \$740.00International preliminary examination fee (37 CFR 1.482) paid to USPTO  
but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . . \$710.00International preliminary examination fee (37 CFR 1.482) paid to USPTO  
and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . . \$100.00**ENTER APPROPRIATE BASIC FEE AMOUNT =**

CALCULATIONS PTO USE ONLY

\$ 890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30  
months from the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS

NUMBER FILED

NUMBER EXTRA

RATE

Total claims

10 - 20 =

x \$18.00

Independent claims

1 - 3 =

x \$84.00

MULTIPLE DEPENDENT CLAIM(S) (if applicable)

+ \$280.00

**TOTAL OF ABOVE CALCULATIONS =**

\$ 890.00

☒ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above  
are reduced by 1/2.**SUBTOTAL =**

\$ 890.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30  
months from the earliest claimed priority date (37 CFR 1.492(f)).**TOTAL NATIONAL FEE =**

\$ 890.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be  
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

40.00

**TOTAL FEES ENCLOSED =**

\$ 930.00

Amount to be  
refunded:

charged:

a. ☐ A check in the amount of \$ \_\_\_\_\_ to cover the above fees is enclosed.b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 930.00 to cover the above fees.  
A duplicate copy of this sheet is enclosed.c. ☐ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any  
overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card  
information should not be included on this form.** Provide credit card information and authorization on PTO-2038.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR  
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:



00157

PATENT TRADEMARK OFFICE

SIGNATURE

Thomas W. Roy

NAME

29,582

REGISTRATION NUMBER

10/019578  
531 Rec'd PCT/ 21 DEC 2001

PATENT APPLICATION  
Mo6862  
LeA 33,590

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

APPLICATION OF )  
LUTZ SCHMALSTIEG ET AL ) PCT/EP00/05392  
SERIAL NUMBER: TO BE ASSIGNED )  
FILED: HEREWITH )  
TITLE: CONDENSATION CROSS-LINKING )  
POLYURETHANE MATERIALS )  
CONTAINING SPECIAL AMINO- )  
SILANES, A METHOD FOR THE )  
PRODUCTION THEREOF AND )  
THEIR USE )

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

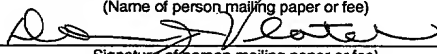
Prior to the examination of the subject application, kindly amend the  
application as follows:

"Express Mail" mailing label number ET700176032US  
Date of Deposit December 21, 2001

I hereby certify that this paper or fee is being deposited with the United States  
Postal Service "Express Mail Post Office to Addressee" service under 37 CFR  
1.10 on the date indicated above and is addressed to the Assistant Commissioner  
of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or fee)

  
Signature of person mailing paper or fee)

IN THE SPECIFICATION:

At page 1, and on page 20 (Abstract) delete the title and insert

--CONDENSATION CROSS-LINKING POLYURETHANE MATERIALS  
CONTAINING SPECIAL AMINOSILANES, A METHOD FOR THE PRODUCTION  
THEREOF AND THEIR USE--.

At page 1, line 3 insert the heading --BACKGROUND OF THE INVENTION--.

Before page 2, line 1 insert the heading --SUMMARY OF THE INVENTION--.

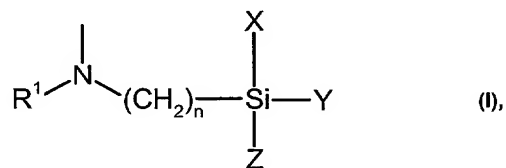
At page 3, line 18 insert the heading --DETAILED DESCRIPTION OF THE  
INVENTION--.

IN THE CLAIMS:

Cancel Claims 1-6.

Kindly add the following claims:

- 7. A polyurethane composition which cross-links via silane  
polycondensation and comprises
- A) at least one alkoxy silane-functional polyurethane having end groups  
corresponding to formula (I)



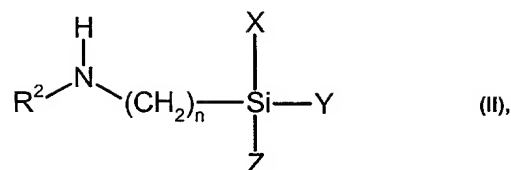
wherein

R<sup>1</sup> represents an organic group having 1 to 12 carbon atoms,

n is an integer from 2 to 4 and

X, Y, Z represent identical or different organic groups, provided that at least one  
of the groups is an alkoxy group having 1 to 4 carbon atoms,

- B) at least one basic filler,
- C) at least one reaction product of
- i) at least one aminosilane corresponding to formula (II)

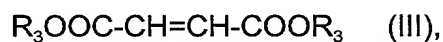


wherein

$\text{R}^2$  represents a hydrogen atom or an aminoethyl group and  
n, X, Y, Z have the meanings set forth for formula (I),

with

ii) at least one maleic or fumaric ester corresponding to formula (III)

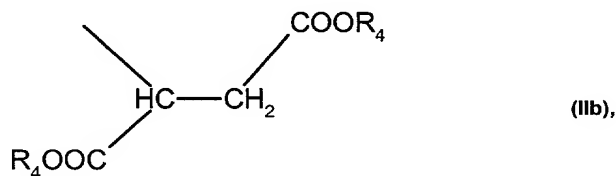


wherein

$\text{R}_3$  represents an alkyl group having 1 to 12 carbon atoms, and

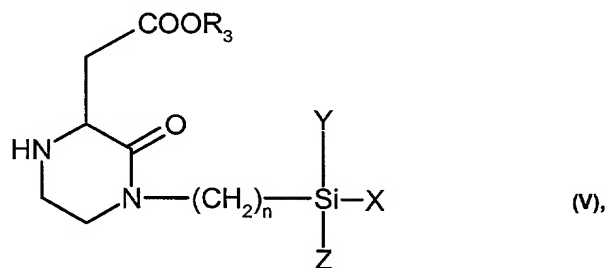
E) at least one organometallic compound.

8. The polyurethane composition of Claim 7 wherein  $\text{R}_1$  represents a group corresponding to formula (IIb)



wherein  $\text{R}_4$  denotes an alkyl group having 1 to 4 carbon atoms.

9. The polyurethane composition of Claim 7 wherein component C) comprises an aminosilane compound corresponding to formula (V)



wherein

R<sub>3</sub> represents a linear or branched aliphatic hydrocarbon group having at most 12 carbon atoms,

n is 3 and

X, Y and Z represent methoxy or ethoxy groups.

10. The polyurethane composition of Claim 7 wherein X, Y and Z each represent a methoxy or ethoxy group.

11. The polyurethane composition of Claim 8 wherein X, Y and Z each represent a methoxy or ethoxy group.

12. The polyurethane composition of Claim 9 wherein X, Y and Z each represent a methoxy or ethoxy group.

13. The polyurethane composition of Claim 7 wherein X, Y and Z each represent a methoxy group in component A).

14. The polyurethane composition of Claim 8 wherein X, Y and Z each represent a methoxy group in component A).

15. The polyurethane composition of Claim 9 wherein X, Y and Z each represent a methoxy group in component A).

16. A process for the preparation of the polyurethane composition of Claim 1 which comprises mixing components A), B), C-i) and E) with exclusion of moisture and subsequently adding component C-ii).--

**REMARKS**

Claims 1-6 have been cancelled and replaced by Claims 7-16. These claims are supported by the original claims. A new abstract is enclosed.

An early action of the merits is respectfully requested.

Respectfully submitted,

By Thomas W. Roy  
Thomas W. Roy  
Attorney for Applicants  
Reg. No. 29,582

Bayer Corporation  
100 Bayer Road  
Pittsburgh, Pennsylvania 15205-9741  
(412) 777-8345  
FACSIMILE PHONE NUMBER:  
(412) 777-8363

/jme/TWR0200

IN THE SPECIFICATION:

At page 1, and on page 20 (Abstract) delete the title and insert

--CONDENSATION CROSS-LINKING POLYURETHANE MATERIALS  
CONTAINING SPECIAL AMINOSILANES, A METHOD FOR THE PRODUCTION  
THEREOF AND THEIR USE--.

At page 1, line 3 insert the heading --BACKGROUND OF THE INVENTION--.

Before page 2, line 1 insert the heading --SUMMARY OF THE INVENTION--.

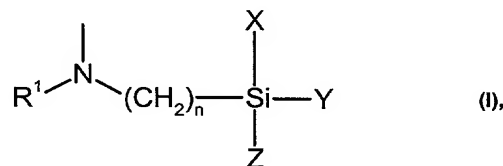
At page 3, line 18 insert the heading --DETAILED DESCRIPTION OF THE  
INVENTION--.

IN THE CLAIMS:

Claims 1-6 were cancelled.

The following claims were added:

- 7. A polyurethane composition which cross-links via silane  
polycondensation and comprises
- A) at least one alkoxy silane-functional polyurethane having end groups  
corresponding to formula (I)



wherein

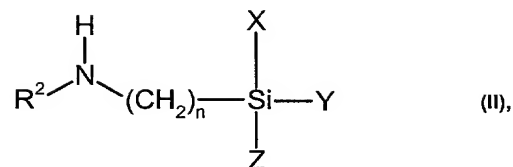
R<sup>1</sup> represents an organic group having 1 to 12 carbon atoms,

n is an integer from 2 to 4 and

X, Y, Z represent identical or different organic groups, provided that at least one  
of the groups is an alkoxy group having 1 to 4 carbon atoms,

- B) at least one basic filler,
- C) at least one reaction product of
- i) at least one aminosilane corresponding to formula (II)



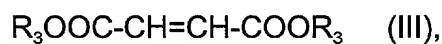


wherein

$\text{R}^2$  represents a hydrogen atom or an aminoethyl group and  
 $n$ ,  $X$ ,  $Y$ ,  $Z$  have the meanings set forth for formula (I),

with

ii) at least one maleic or fumaric ester corresponding to formula (III)

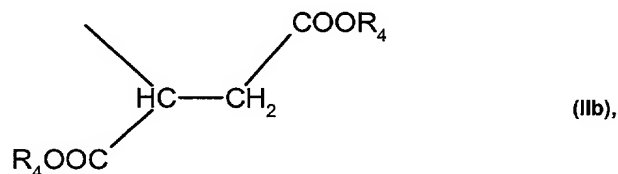


wherein

$\text{R}_3$  represents an alkyl group having 1 to 12 carbon atoms, and

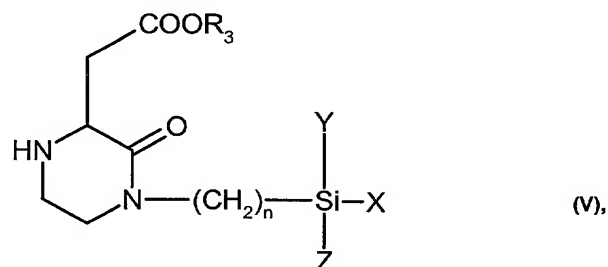
E) at least one organometallic compound.

8. The polyurethane composition of Claim 7 wherein  $\text{R}_1$  represents a group corresponding to formula (IIb)



wherein  $\text{R}_4$  denotes an alkyl group having 1 to 4 carbon atoms.

9. The polyurethane composition of Claim 7 wherein component C) comprises an aminosilane compound corresponding to formula (V)



wherein

$R_3$  represents a linear or branched aliphatic hydrocarbon group having at most 12 carbon atoms,

n is 3 and

X, Y and Z represent methoxy or ethoxy groups.

10. The polyurethane composition of Claim 7 wherein X, Y and Z each represent a methoxy or ethoxy group.

11. The polyurethane composition of Claim 8 wherein X, Y and Z each represent a methoxy or ethoxy group.

12. The polyurethane composition of Claim 9 wherein X, Y and Z each represent a methoxy or ethoxy group.

13. The polyurethane composition of Claim 7 wherein X, Y and Z each represent a methoxy group in component A).

14. The polyurethane composition of Claim 8 wherein X, Y and Z each represent a methoxy group in component A).

15. The polyurethane composition of Claim 9 wherein X, Y and Z each represent a methoxy group in component A).

16. A process for the preparation of the polyurethane composition of Claim 1 which comprises mixing components A), B), C-i) and E) with exclusion of moisture and subsequently adding component C-ii).--

- 20 -

CONDENSATION CROSS-LINKING POLYURETHANE MATERIALS  
CONTAINING SPECIAL AMINOSILANES, A METHOD FOR THE  
PRODUCTION THEREOF AND THEIR USE

Abstract

This invention relates to polyurethane compositions which cross-link via a silane polycondensation and contain at least one alkoxy silane-functional polyurethane, at least one basic filler, at least one reaction product of an aminosilane with a maleic or fumaric ester, at least one organometallic compound and optionally additional auxiliary substances, to a process for their preparation, and to their use.

10/019578

531 Rec'd PCT 21 DEC 2001

**Special polyurethane compositions which cross-link by condensation and contain aminosilanes, a process for their preparation and their use**

5 This invention relates to polyurethane compositions which cross-link via a silane polycondensation and contain at least one alkoxysilane-functional polyurethane, at least one basic filler, at least one reaction product of an aminosilane with a maleic or fumaric ester, at least one organometallic compound and optionally additional auxiliary substances, to a process for their preparation, and to their use.

10 Alkoxysilane-functional polyurethanes which cross-link via a silane polycondensation are part of long-known prior art. A survey of the topic is to be found in "Adhesives Age" 4/1995, page 30 ff. (authors: Ta-Min Feng, B. A. Waldmann). Such alkoxysilane-terminated, moisture-curing one-component polyurethanes are increasingly being used as flexible elastic coating, sealing and adhesive compositions in the construction  
15 industry and in the automobile industry. For these applications, high demands are placed on the extensibility, the adhesive power and on the speed of cure.

Such products are described by way of example in EP-A 596360, EP-A 831108, EP-A 807649 or in EP-A 676403. Organometallic catalysts as well as adhesion promoters of  
20 the aminosilane type are commonly used concomitantly in the formulation of systems of this kind. But the addition of aminosilane compounds can often lead to problems with stability in storage, particularly when higher proportions of aminosilanes are used in order to achieve a good adhesion to difficult substrates.

25 Accordingly, the object of the present invention was to provide polyurethane compositions which cross-link via a silane polycondensation, contain aminosilanes and have an improved stability in storage.

30 This object was achieved by the provision of the polyurethane compositions which cross-link by condensation described in more detail below.

"Express Mail" mailing label number ET700176032US

Date of Deposit December 21, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

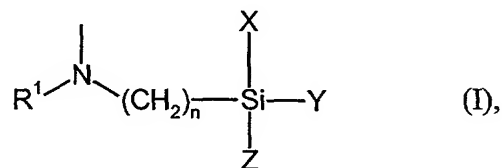
(Name of person mailing paper or fee)



(Signature of person mailing paper or fee)

The invention provides polyurethane compositions which cross-link via a silane polycondensation, containing

- A) at least one alkoxy silane-functional polyurethane having end groups corresponding to the general formula (I)



wherein

$\text{R}^1$  represents an organic group having 1 to 12 carbon atoms,

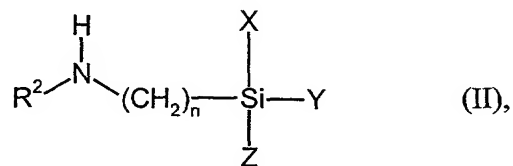
$n$  is an integer from 2 to 4

and

$\text{X, Y, Z}$  denote identical or different organic groups, with the proviso that at least one of the groups is an alkoxy group having 1 to 4 carbon atoms, preferably a methoxy or ethoxy group,

- B) at least one basic filler,

- C) at least one reaction product of at least one aminosilane corresponding to the general formula (II)

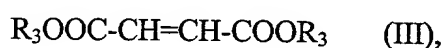


wherein

$R^2$  represents a hydrogen atom, or an aminoethyl group and

n, X, Y, Z have the meanings given for formula (I),

with at least one maleic or fumaric (ester) corresponding to the general formula (III)



wherein

$R_3$  represents an alkyl group having 1 to 12 carbon atoms,

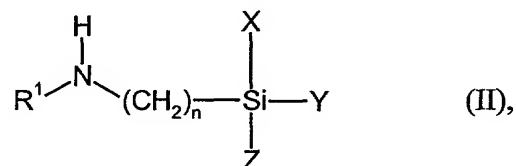
E) at least one organometallic compound and

F) optionally additional auxiliary substances.

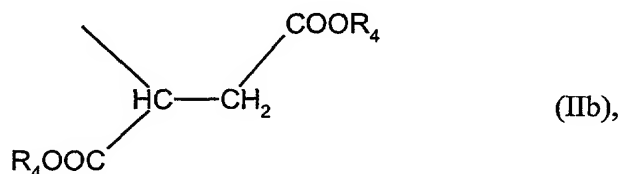
The invention is based on the surprising observation that the adducts of aminosilanes with maleic or fumaric esters which, according to the invention, are used instead of the aminosilanes conventionally employed as adhesion promoters, bring about improved mechanical properties and an improved stability in storage.

The reaction products of maleic or of fumaric esters and aminosilanes which according to the invention are to be used as component C) are known in principle and are described by way of example in EP-A 596360 or EP-A 831108. According to the disclosures in these publications, the reaction products of maleic or of fumaric esters with aminosilanes are used for the reaction with isocyanate prepolymers. The use of these products as an additive for improving the mechanical properties and for improving the adhesion of polyurethanes which cross-link via silane polycondensation is hitherto unknown.

The polyurethanes having alkoxy silane end groups which according to the invention are to be used as component A) are known in principle and are prepared by reacting long-chain, preferably linear, NCO prepolymers with aminofunctional silanes corresponding to the general structural formula (II)



wherein  $\text{R}^1$  represents an organic group having 1 to 12 carbon atoms, preferably a phenyl group or particularly preferably a group corresponding to the general structural formula (IIb),



wherein  $\text{R}_4$  represents an alkyl group having 1 to 4 carbon atoms. In the above structural formula,  $n$  is an integer from 2 to 4, preferably 3.

$\text{X}$ ,  $\text{Y}$ ,  $\text{Z}$  in the above structural formula denote identical or different organic groups, with the proviso that at least one of the groups is an alkoxy group having 1 to 4 carbon atoms. Preferably at least one of the groups is a methoxy or ethoxy group. Particularly preferably  $\text{X}$ ,  $\text{Y}$  and  $\text{Z}$  each represent a methoxy group.

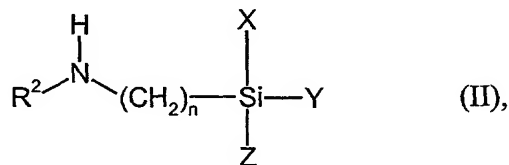
Examples of suitable aminofunctional silanes corresponding to structural formula (I) are N-methyl-3-aminopropyltrimethoxysilane, N-methyl-3-aminopropyltriethoxysilane, N-butyl-3-aminopropyltrimethoxysilane. The use of N-phenyl-3-aminopropyltrimethoxysilane is preferred. It is particularly preferable to use the aspartic esters

described in EP-A 596360, which are formed through the reaction of aminosilanes corresponding to the general structural formula (II) with maleic or fumaric esters corresponding to formula (III).

5 NCO prepolymers which can be used for the preparation of the polyurethanes A) having alkoxy silane end groups are prepared in known per se manner by reacting polyether polyols, preferably polyether diols, with diisocyanates and have an NCO content of between 0.4 and 4%.

10 Compounds which can be used as basic fillers B) are precipitated or ground chalks, metal oxides, metal sulfates, metal silicates, metal hydroxides, metal carbonates and metal hydrogen carbonates. Other fillers are, for example, reinforcing and non-reinforcing fillers such as, for example, pyrogenic or precipitated silicas, carbon black or quartz powder. Both the basic fillers and the other reinforcing or non-reinforcing  
15 fillers may optionally be surface-modified. Precipitated or ground chalks and pyrogenic silicas are particularly preferably used as basic fillers B). The component B) may, of course, also be mixtures of fillers.

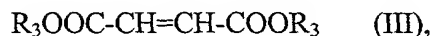
20 Compounds used as component C) are reaction products of aminosilane compounds corresponding to the general structural formula (II)



wherein

25  $\text{R}^2$ , X, Y, Z and n have the meanings given above,

with maleic or fumaric (esters) corresponding to the general formula (III)





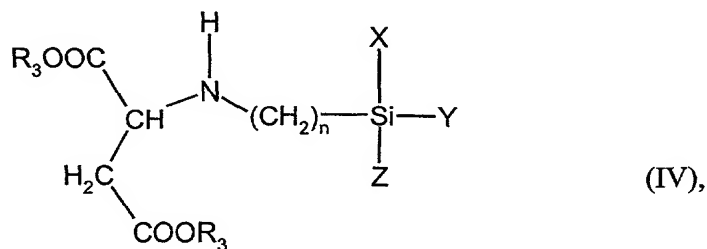
wherein

$R_3$  represents an alkyl group having 1 to 12 carbon atoms.

5 Examples of usable aminosilane compounds corresponding to formula (II) are 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, N-aminoethyl-3-aminopropyltrimethoxysilane, N-aminomethyl-3-aminopropyltriethoxysilane, 3-aminopropylmethyldiethoxysilane and N-aminoethyl-3-aminopropylmethyldimethoxysilane.

10 In formula (III),  $R_3$  represents a linear or branched aliphatic hydrocarbon group having at most 12 carbon atoms. Examples of suitable maleic and fumaric esters are diethyl maleate, dimethyl maleate, dibutyl maleate, dioctyl maleate, diethyl fumarate, dimethyl fumarate, dioctyl fumarate.

15 In the case where the products in which  $R_2$  in formula (II) denotes a hydrogen atom are used as aminosilanes, in the course of the reaction with the maleic or fumaric esters in accordance with the disclosure in EP-A 596360, aspartic esters corresponding to the general structural formula (IV) are formed



20

wherein

$R^3$ , X, Y, Z and n have the meanings given for formulae (II) and (III).

25 In the particularly preferred case, where products in which  $R_2$  denotes an aminoethyl group are used as aminosilanes corresponding to formula (II), piperazinone derivatives corresponding to the general formula (V)



wherein

5 R<sub>3</sub>, X, Y, Z and n have the meanings given for formula (IV),

are formed through a cyclocondensation reaction.

10 densation, can be used as component E). These are in particular compounds of tin and  
of titanium. Preferred tin compounds are, for example, dibutyltin dilaurate, dibutyltin  
diacetate and dioctyltin maleate, tin(II) octoate or dibutyltin bis(acetoacetate).  
Preferred titanium compounds are, for example, alkyl titanates, such as tetraisopropyl  
titanate, tetrabutyl titanate and chelated titanium compounds, such as ethyl  
15 diisobutylbis(acetoacetate) titanate. Dibutyltin bis(acetoacetate) is particularly  
preferably used as component E).

Additives and auxiliary substances F) according to the invention which may be mentioned are drying agents, plasticisers, adhesives other than those mentioned under 20 D), thixotropic agents, light stabilisers, pigments and protective agents, for example, fungicides.

vinyltrimethoxysilane, methyltrimethoxysilane, i-butyltrimethoxysilane, hexadecyl-  
25 trimethoxysilane. Examples of plasticisers which may be given are phthalic esters,  
adipic esters, alkylsulfonic esters of phenol or phosphate esters. Examples of  
thixotropic agents which may be given are polyamides, hydrogenated products of

castor oil or even polyvinyl chloride. Aminosilanes of the known kind, epoxysilanes and/or mercaptosilanes can be used as adhesion promoters in addition to the compounds mentioned under C).

- 5 The polyurethane compositions according to the invention consist preferably of 30 to 80 wt.% of component A), 10 to 50 wt.% of component B), 0.5 to 3 wt.% of component C), 0.02 to 1 wt.% of component D) and 0 to 40 wt.% of component F).

10 The present invention also provides a process for the preparation of the polyurethane compositions according to the invention which cross-link by condensation. In the process according to the invention, component C) is prepared in a separate reaction vessel by reacting the aminosilanes with the maleic or fumaric esters, similarly to the disclosure in EP-A 596360, in the temperature range of 0°C to 100°C. Components A), B), D) and optionally E) are mixed together, with exclusion of moisture, and  
15 component C) is then added thereto.

In a preferred embodiment of the process according to the invention, the component C) used according to the invention is produced in situ. In this procedure, components A), B), D) and optionally E), together with the maleic or fumaric esters used for the  
20 preparation of C), are mixed together, with exclusion of moisture, and the aminosilanes used according to the invention to prepare component C) are then added thereto.

The present invention also provides the use of the reaction products of aminosilanes and maleic and fumaric esters, which can be used according to the invention as  
25 component C), as an additive in polyurethane compositions which cross-link by condensation.

The present invention further provides the use of the polyurethane compositions according to the invention which cross-link by condensation as sealant, adhesive or  
30 coating material.

The polyurethane compositions according to the invention which cross-link by condensation on the one hand exhibit a rapid cure with skin formation times of between 15 and 120 minutes, but on the other hand have excellent stability in storage in the temperature range of up to 60°C.

5

The cross-linked polymers exhibit improved mechanical properties, in particular an improved elongation at tear as compared with similar systems containing conventional aminosilanes. Moreover, the polyurethane compositions according to the invention are distinguished by having excellent adhesion, in particular wet adhesion, to all conceivable substrates such as, for example, metal, ceramic, plastics, stone or concrete.

10

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## Examples

### Preparation of a polyurethane A1) having alkoxysilyl end groups

5        2000 g of a polyether diol having an OH value of 28, prepared by propoxylation of propylene glycol and subsequent ethoxylation of the propoxylation product (PO/EO ratio = 80:20), was prepolymerised with 155.4 g isophorone diisocyanate at 70°C, with addition of 0.02 g dibutyltin dilaurate, until the theoretical NCO content of 0.78% was attained. The reaction mixture was cooled to 60°C, then 140.4 g N-(3-  
10       trimethoxysilylpropyl)aspartic acid, diethyl ester (prepared as in EP-A 596360, Example 5) was added speedily and the mixture stirred until isocyanate bands were no longer to be seen in the IR spectrum. The resulting polyurethane prepolymer with alkoxysilyl end groups had a viscosity of 76000 mPas (23°C).

### 15       Preparation of a polyurethane A2) having alkoxysilyl end groups

2000 g of a polyether diol having an OH value of 28, prepared by propoxylation of propylene glycol and subsequent ethoxylation of the propoxylation product (PO/EO ratio = 80:20), was prepolymerised with 155.4 g isophorone diisocyanate at 70°C, with  
20       addition of 0.02 g dibutyltin dilaurate, until the theoretical NCO content of 0.78% was attained. The reaction mixture was cooled to 60°C, then 102 g N-phenyl-3-aminopropyltrimethoxysilane was added speedily and the mixture stirred until isocyanate bands were no longer to be seen in the IR spectrum. The resulting polyurethane prepolymer with alkoxysilyl end groups had a viscosity of 86000 mPas  
25       (23°C).

**Example 1**

**Preparation of a polyurethane composition according to the invention**

5 In a commercial planetary mixer, the following components were processed to produce a ready-to-use sealant:

	36.4 parts by wt.	polyurethane A1)
	12.9 parts by wt.	diisoundecyl phthalate (plasticiser)
10	0.02 parts by wt.	dibutyltin bis(acetoacetate) (10% dissolved in solvent naphtha 100)
	1.50 parts by wt.	vinyltrimethoxysilane
	46.2 parts by wt.	precipitated chalk (type: Socal® U1S2)
	2.00 parts by wt.	diethyl maleate
15	1.40 parts by wt.	Disparlon® NVG8403 S (thixotropic agent from Kusumoto Chem. Ltd.)

The mixture was dispersed for 10 minutes at a pressure of 100 mbar, during which the internal temperature rose to 60°C. Then

20 1.5 parts by wt. N-aminoethyl-3-aminopropyltrimethoxysilane

was added and worked in by stirring for 10 minutes at a pressure of 100 mbar. The sealant thus prepared had excellent stability, bonded to virtually all substrates and cured

25 with a skin formation time of 30 minutes.

The product was packed into a commercial cartridge and stored at 50°C. After a storage period of 90 days, the product could still be processed without difficulty and exhibited no changes in its properties.

30 The following mechanical properties were determined:

Tensile strength	2.6 N/mm <sup>2</sup>	(DIN 53504)
Elongation at break	268%	(DIN 53504)
Tear propargation resistance	5.4 N/mm	(DIN 53515)
Shore A hardness	42	

5

## Example 2

### Preparation of a polyurethane composition according to the invention

10 In a commercial planetary mixer, the following components were processed to produce a ready-to-use sealant:

	36.0 parts by wt.	polyurethane from Example 2
	12.6 parts by wt.	diisoundecyl phthalate (plasticiser)
15	0.02 parts by wt.	dibutyltin bis(acetoacetate) (10% dissolved in solvent naphtha 100)
	2.20 parts by wt.	vinyltrimethoxysilane
	45.68 parts by wt.	precipitated chalk (type: Socal® U1S2 from Solvay GmbH)
	2.00 parts by wt.	dimethyl maleate
20	1.40 parts by wt.	Cabosil® TS 720 (pyrogenic silica from Cabot GmbH)

The mixture was dispersed for 10 minutes at a pressure of 100 mbar, during which the internal temperature rose to 60°C. Then

25 2.1 parts by wt. N-aminoethyl-3-aminopropyltrimethoxysilane

was added and worked in by stirring for 10 minutes at a pressure of 100 mbar.

30 The sealant thus prepared had excellent stability, bonded to virtually all substrates and cured with a skin formation time of 40 minutes.

The product was packed into a commercial cartridge and stored at 50°C. After a storage period of 90 days, the product could still be processed without difficulty and exhibited no changes in its properties.

5 The following mechanical properties were determined:

Tensile strength	2.8 N/mm <sup>2</sup>	(DIN 53504)
Elongation at break	290%	(DIN 53504)
Tear propargation resistance	7.5 N/mm	(DIN 53515)
Shore A hardness	46	

10

### **Example 3**

#### **Comparison Example not according to the invention**

15 Example 1 was repeated, with the difference that no diethyl maleate was added. The product was packed into a commercial cartridge and stored at 50°C. After a storage period of 60 days, the product could no longer be squeezed out of the cartridge and had gelled.

20 The following mechanical properties were determined:

Tensile strength	2.5 N/mm <sup>2</sup>	(DIN 53504)
Elongation at break	235%	(DIN 53504)
Tear propargation resistance	5.6 N/mm	(DIN 53515)
Shore A hardness	42	

25

### **Example 4**

#### **Comparison Example not according to the invention**

30 Example 2 was repeated, with the difference that no dimethyl maleate was added. The product was packed into a commercial cartridge and stored at 50°C. After a storage



period of 35 days, the product could no longer be squeezed out of the cartridge and had gelled.

The following mechanical properties were determined:

5	Tensile strength	2.8 N/mm <sup>2</sup>	(DIN 53504)
	Elongation at break	250%	(DIN 53504)
	Tear propargation resistance	7.4 N/mm	(DIN 53515)
	Shore A hardness	46	

## 10 Example 5

### Preparation of a polyurethane composition according to the invention

15 In a commercial planetary mixer, the following components were processed to produce a ready-to-use sealant:

	36.4 parts by wt.	polyurethane A1)
	12.9 parts by wt.	diisoundecyl phthalate (plasticiser)
	0.04 parts by wt.	dibutyltin bis(acetoacetate) (10% dissolved in solvent naphtha
20		100)
	1.50 parts by wt.	vinyltrimethoxysilane
	46.2 parts by wt.	precipitated chalk (type: Socal® U1S2)
	1.40 parts by wt.	Disparlon® NVG8403 S (thixotropic agent from Kusumoto
		Chem. Ltd.)

25 The mixture was dispersed for 10 minutes at a pressure of 100 mbar, during which the internal temperature rose to 60°C. Then

30	2.5 parts by wt.	N-(3-trimethoxysilylpropyl)aspartic acid, diethyl ester (prepared as in EP-A 596360, Example 5)
----	------------------	--

was added and worked in by stirring for 10 minutes at a pressure of 100 mbar.

The sealant thus prepared had excellent stability, bonded to virtually all substrates and cured with a skin formation time of 50 minutes.

5

The product was packed into a commercial cartridge and stored at 50°C. After a storage period of 90 days, the product could still be processed without difficulty and exhibited no changes in its properties.

10 The following mechanical properties were determined:

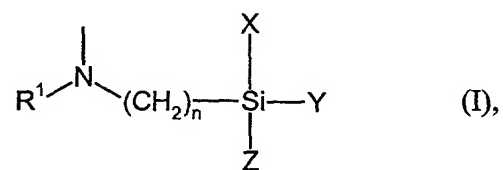
Tensile strength	2.5 N/mm <sup>2</sup>	(DIN 53504)
Elongation at break	310%	(DIN 53504)
Tear propargation resistance	6.1 N/mm	(DIN 53515)
Shore A hardness	39	

Claims

1. Polyurethane compositions which cross-link via a silane polycondensation, containing

5

- A) at least one alkoxy silane-functional polyurethane having end groups corresponding to the general formula (I)



10

wherein

$\text{R}^1$  represents an organic group having 1 to 12 carbon atoms,

15

$n$  is an integer from 2 to 4

and

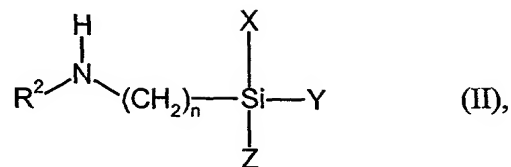
20

$\text{X}, \text{Y}, \text{Z}$  denote identical or different organic groups, with the proviso that at least one of the groups is an alkoxy group having 1 to 4 carbon atoms, preferably a methoxy or ethoxy group,

25

- B) at least one basic filler,
- C) at least one reaction product of at least one aminosilane corresponding to the general formula (II)

- 17 -

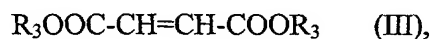


wherein

$\text{R}^2$  represents a hydrogen atom, or an aminoethyl group and

$n, X, Y, Z$  have the meanings given for formula (I),

with at least one maleic or fumaric (ester) corresponding to the general formula (III)



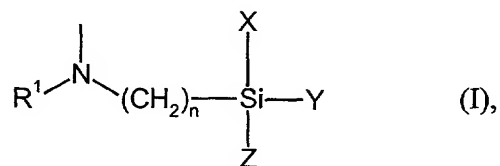
wherein

$\text{R}_3$  represents an alkyl group having 1 to 12 carbon atoms,

E) at least one organometallic compound and

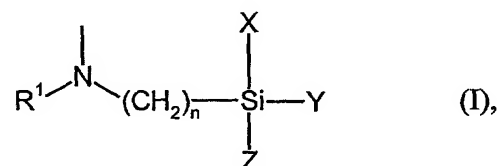
F) optionally additional auxiliary substances.

2. Polyurethane compositions which cross-link via a silane polycondensation according to claim 1, characterised in that at least one alkoxysilyl-functional polyurethane corresponding to the general formula (I)

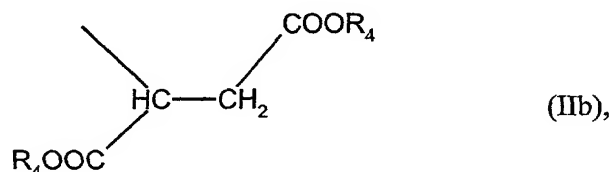


wherein X, Y and Z each represent a methoxy group, is used as component A).

3. Polyurethane compositions which cross-link via a silane polycondensation according to claims 1 and 2, characterised in that at least one alkoxyethyl-functional polyurethane corresponding to the general formula (I)

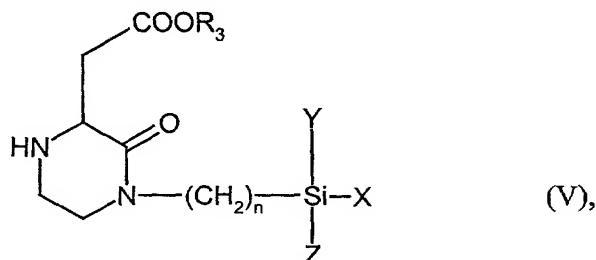


wherein  $\text{R}_1$  represents a group corresponding to the general formula (IIb)



wherein  $\text{R}_4$  denotes an alkyl group having 1 to 4 carbon atoms, is used as component A).

4. Polyurethane compositions which cross-link via a silane polycondensation according to claim 1, characterised in that aminosilane compounds corresponding to the general formula (V)



wherein

$R_3$  represents a linear or branched aliphatic hydrocarbon group having at most 12 carbon atoms, n is 3 and X, Y, Z represent methoxy or ethoxy groups,

5 are used as component D).

5. Process for the preparation of the polyurethane compositions which cross-link by condensation according to claim 1, wherein components A), B), C), E) and optionally F) are mixed together, with exclusion of moisture, and component  
10 D) is then added thereto.

6. Use of the polyurethane compositions which cross-link by condensation according to claim 1 as sealant, adhesive or coating material.

**COMBINED DECLARATION AND POWER OF ATTORNEY**

ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled

**CONDENSATION CROSS-LINKING POLYURETHANE MATERIALS CONTAINING SPECIAL AMINOSILANES, A METHOD FOR THE PRODUCTION THEREOF AND THEIR USE**

the specification of which is attached hereto,

or was filed on **June 13, 2000**

as a PCT Application Serial No. **PCT/EP00/05392**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

<b>199 29 011.3</b> (Number)	<b>Germany</b> (Country)	<b>June 25, 1999</b> (Month/Day/Year Filed)
<b>199 29 029.6</b> (Number)	<b>Germany</b> (Country)	<b>June 25, 1999</b> (Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)

[illegible]

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**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following attorney(s) and this application and to transact all business in the Patent and Trademark Office conne

JOSEPH C. GIL, Patent Office Registration Number 26,602 ARON PREIS, Patent Office Registration Number 29,426  
LYNDANNE M. WHALEN, Patent Office Registration Number 29,457 THOMAS W. ROY,  
Patent Office Registration Number 29,582 RICHARD E. L. HENDERSON, Patent Office Registration Number 31,619  
GODFRIED R. AKORLI, Patent Office Registration Number 28,779 N. DENISE BROWN, Patent Office  
Registration Number 36,097 NOLAND J. CHEUNG, Patent Office Registration Number 39,138  
DIDERICO VAN EYL, Patent Office Registration Number 38,641 CAROLYN M. SLOANE, Patent Office  
Registration Number 44,339 JAMES R. FRANKS, Patent Office Registration Number 42,552  
JACKIE ANN ZURCHER, Patent Office Registration Number 42,251  
RAYMOND J. HARMUTH, Patent Office Registration Number 33,896  
all of Bayer Corporation, Pittsburgh, Pennsylvania 15205-9741

13

Send Correspondence To: Direct Telephone Calls To:  
Patent Department  
Bayer Corporation (412) 777-2349  
100 Bayer Road  
Pittsburgh, Pennsylvania 15205-9741

FULL NAME OF SOLE OR FIRST INVENTOR Lutz Schmalstieg		INVENTOR'S SIGNATURE <i>[Signature]</i>	DATE 2001-10-09
RESIDENCE D 50676 Köln, Germany		CITIZENSHIP German	
POST OFFICE ADDRESS Schnurgasse 45, D 50676 Köln, Germany			
FULL NAME OF SECOND INVENTOR Ralf Lemmerz		INVENTOR'S SIGNATURE <i>[Signature]</i>	DATE 04 Oct 2001
RESIDENCE D 51375 Leverkusen, Germany		CITIZENSHIP German	
POST OFFICE ADDRESS c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany			
FULL NAME OF THIRD INVENTOR Ulrich Walter (deceased)		INVENTOR'S SIGNATURE	DATE
RESIDENCE D 40764 Langenfeld, Germany		CITIZENSHIP German	
POST OFFICE ADDRESS Zum Galkhausener Bach 17, D 40764 Langenfeld, Germany			
FULL NAME OF THE HEIR OF THIRD INVENTOR Marie-Hélène Marie-Ange Christiane Walter		SIGNATURE <i>[Signature]</i>	DATE 22 Oct 01
RESIDENCE D 40764 Langenfeld, Germany		CITIZENSHIP French	
POST OFFICE ADDRESS Zum Galkhausener Bach 17, D 40764 Langenfeld, Germany			
FULL NAME OF FOURTH INVENTOR Oswald Wilmes		INVENTOR'S SIGNATURE <i>[Signature]</i>	DATE 2001-10-15
RESIDENCE D 51061 Köln, Germany		CITIZENSHIP German	
POST OFFICE ADDRESS c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany			
FULL NAME OF SIXTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SEVENTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			